

Ohmic drops in the ion-exchange bed of cationic electrodeionisation cells

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Abstract

The work was aimed at investigating the ohmic drop in ion-exchanging resin beds in EDI cells, by using two techniques. The case of $\text{CuSO}_4\text{-H}_2\text{SO}_4$ solutions was treated here, using Dowex resins of various degrees of cross-linking. Impedance measurements in a dedicated cell filled with resin packed beds were interpreted by using a model for the conductivity of two-phase media. Secondly, the voltage recorded in a small EDI cell for continuous treatment of copper solutions, led to the bed conductivity, using a model for potential distribution in the cell. The consistency of the two techniques was discussed, and side electrical phenomena in the EDI cell were shown to be the source of an unexpectedly significant increase in the cell voltage.

Abbreviation

Symbols

a	parameter in Wyllie's model
b	parameter in Wyllie's model
c	parameter in Wyllie's model
d	parameter in Wyllie's model
d_b	width of the bed (m)
d_e	width of the electrode chamber (m)
e	parameter in Wyllie's model
I	current (A)
L	electrode gap in the conductivity cell (m)
l_b	height of the ion exchange resin bed (m)
l_e	electrode length in the EDI cell (m)
R	resistance (Ω)
R_b	resistance of the bed (Ω)
S	cross-sectional area (m^2)
U_{cell}	cell voltage (V)
U_{ohm}	ohmic drop (V)
U_0	equilibrium cell voltage (V)
w	depth of the cell (m)
x	coordinate, along the current
y	coordinate, normal to the current

η	overvoltage (V)
κ	electrical conductivity of the liquid (S m^{-1} , or mS cm^{-1})
κ_e	conductivity of the sulphuric solution (S m^{-1} , or mS cm^{-1})
$\bar{\kappa}$	electrical conductivity of the solid (S m^{-1} , or mS cm^{-1})
κ_b	electrical conductivity of the bed (S m^{-1} , or mS cm^{-1})
Φ	potential (V)
Φ_{cell}	Potential difference in the cell, used for primary distributions (V)

Subscripts

a	anode
av	average
b	bed
c	cathode
e	electrode
in	inlet conditions
out	outlet conditions

1. Introduction

Dilute solutions of heavy/transition metals can be treated by a combination of electrodialysis and ion exchange [1–3]. The solution to be treated is injected

continuously through a packed-bed of ion exchange resins inserted between two electrode compartments, separated by ion-selective membranes. Metal cations are sorbed by the resins, and are transported to the cathode compartment under the action of the applied electrical

field. This technique, also called electrodeionisation (EDI) was shown to be efficient for treatment of dilute solutions of nickel or copper ions [4, 5].

Ion-exchange resins are polymers that have fixed ionic sites prone to reaction with free ions of the opposite charge. The ionic groups of the resin provide a location at which the dissolved ions can be exchanged. Ion-exchange resins in electrolyte solutions are electrically conductive, and counter ions can transfer across the polymer under an electric field, allowing mass transfer and associated current flow. The electrical conductivity of ion-exchange resins varies with the mobility and affinity of the counter ions with which the resins are in contact [6]. In the case of very low specific conductivity of interstitial solution, the specific conductivity of the bed is enhanced by the presence of ion exchange resins. Therefore, the main advantage of using ion exchange resins in the diluate compartment is the substantial reduction in electrical resistance allowed when very low concentration solutions are concerned. This is especially useful in EDI for ultrapure water production. In contrast to EDI, electrodialysis would be inefficient due to the high resistivity of water.

Although ion-exchange resins play a significant role in the EDI process and, in spite of the appreciable ohmic drops in packed beds, the electrical features of ion-exchange resins have been little investigated. This work was aimed at investigating the electrical behaviour of a small packed-bed of resins, with particular emphasis on its overall conductivity. The case of copper sulphate solutions using Dowex resins of different cross-linking degrees is treated here. The electrical conductivity of ion exchange resins was determined by measurement of the impedance of a lab cell with two facing Pt sheets. Data for EDI experiments for removal of copper ions were also exploited for further estimation of the bed conductivity.

2. Models for electrical conductivity of resin beds

Electrical conductivity of packed beds of resins is complex because of the presence of two conducting

phases, namely the resin and the continuous phase. In addition, in contrast to the case of packed beds of solid inert particles, the geometrical, electrical and chemical properties of ion exchange beads are sensitive to the chemical composition of the liquid, continuous phase, as adsorption equilibrium prevails. First attempts in modelling often involved regular lattice arrangements, such as that suggested by Baron who considered a statistical cage model [6]. However, most approaches were not valid for resin particles in contact with one another. A more realistic model was developed decades ago by Wyllie et al. [7], and relies upon the “porous-plug” model described below. The electrical current is considered to pass through three different paths within the bed: (i) through alternating layers of particles and interstitial solution, (ii) through particles in contact with each another, and in the channel of the liquid phase (iii). In most cases, process (i) predominates; however the contribution of (ii) is significant for low-conductivity liquids. The principle can be depicted in terms of electrical resistances in parallel, as shown in Figure 1, each corresponding to one type of conduction.

From the electrical circuit, the electrical conductivity of the bed, κ_b , is the sum of the three contributions,

$$\kappa_b = \frac{a\kappa \bar{\kappa}}{d\kappa + e\bar{\kappa}} + b\bar{\kappa} + c\kappa \tag{1}$$

where κ and $\bar{\kappa}$ are the conductivities of the liquid and solid phase, respectively, and parameters a , b and c , are the fractional cross-section equivalents of the three elements:

$$a + b + c = 1 \tag{2}$$

The denominator of the first right term expresses the contribution of the liquid, with weight d , and of the solid, weight e in the first conduction process. Parameters d and e obey the relation:

$$d + e = 1 \tag{3}$$

Parameters a , b , and c of the three elements, and contributions d and e to the first element are empirical

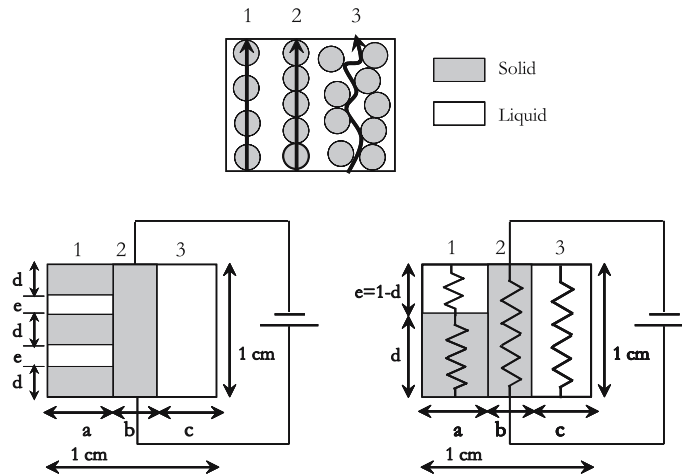


Fig. 1. The “porous-plug” model [7]. Top: schematic representation of the three paths for the current. Left bottom, simplified model consisting in three conductance elements in parallel. Right bottom, extension of the model.

constants which must be determined experimentally. The parameters of the model were estimated to predict the electrochemical properties of the resins.

3. Measurements of the electrical conductivity in a laboratory cell

3.1. Experimental section

Three ion-exchange resins (Dowex) with cross-linking degree of 2, 4 and 8 DVB% were investigated. Particle sizes ranged from 0.15 to 0.30 mm for grades 50 WX 2% and 50 WX 4%, and HCR-S 8% particles had a diameter in the range 0.30–0.84 mm. The capacity of resins beds was measured at 0.756, 1.17 and 1.81 eq l⁻¹ for the 8, 4 and 2% grade, respectively. Resins were tested under the H⁺ or Cu²⁺ form: Cu²⁺ form resins were prepared by impregnation of H⁺ form sorbents in a column upon continuous percolation by an excess 0.25 M CuSO₄ solution. Percolation of the resins with a large volume of 0.25 M sulphuric acid allows their complete conversion to the H⁺-form. For both cases, the resins were thoroughly rinsed with deionised water. The conductivity of H⁺ resins was measured in dilute sulphuric solutions, while Cu²⁺ resins were investigated in copper sulphate solutions.

Conductivity measurements were carried out in a cubic cell 2 cm in dimensions. Flat platinum electrodes 2×2 cm² were fixed at two opposite inner walls of the cell. The electrodes were connected to an Autolab PGSTAT 20 potentiostat with a sine function generator. The cell was first filled with the liquid phase using a polyethylene syringe and the electrochemical impedance was measured at zero cell voltage. The voltage amplitude was 5 mV and the frequency of the signal varied from 30 kHz to 30 Hz, with ten points per decade. The amount of liquid introduced was determined accurately, taking into account the meniscus of the G/L interface, corresponding to an excess of liquid. The error involved in filling the cell was estimated at approx. 2% in the 8 cm³ cell volume. After measurement of the liquid conductivity, the resin was introduced to the cell, and the bed was compacted by vibrating the cell; the excess liquid was removed using a syringe. Compact beds of resins were obtained after the top shiny surface of the liquid over the packed bed disappeared and was replaced by the granular, irregular surface of the bed of resin particles, uncovered by the liquid. Impedance spectra were then recorded. The formerly used solution was thereafter diluted with pure water by 20–30% and the resins were rinsed in the obtained liquid. The experimental procedure of successive measurements with the liquid, then with the resin bed, was repeated. Solutions were progressively diluted until their conductivity was of the order of 10⁻⁴ S cm⁻¹.

The intercept of the impedance spectrum recorded at rest potential with the real axis led to the ohmic

resistance, and the conductivity of the medium was deduced using the relation:

$$\kappa = \frac{1}{R} \frac{L}{S} \quad (4)$$

Here L is the electrode gap, 2 cm, and S is the electrode area. The cell was calibrated and the l/S ratio was taken at 0.52 cm⁻¹ instead of 0.50 cm⁻¹.

Experiments conducted with packed beds of inert resins of the same diameter, with conducting solutions allowed estimation of the parameter c . Numerous measurements conducted with the two softest resins led to $c = 0.28$, in agreement with the value obtained by Martin et al. from modelling of heat transfer in packed beds [8], with a liquid void fraction of 40%.

3.2. Experimental results

Figure 2 shows the conductivity of the cation exchange resin beds versus the conductivity of the interstitial solution. The variation depends on the nature of the electrolyte and the resin grade, as expected. Although low, the bed conductivity with pure water was not negligible and was due to the solid conductivity, $\bar{\kappa}$. The conductivity of the bed impregnated with dilute solution increased rapidly and was far larger than that of the liquid: ions are mainly transferred by the solid phase. The difference between κ_b and κ decreased for higher

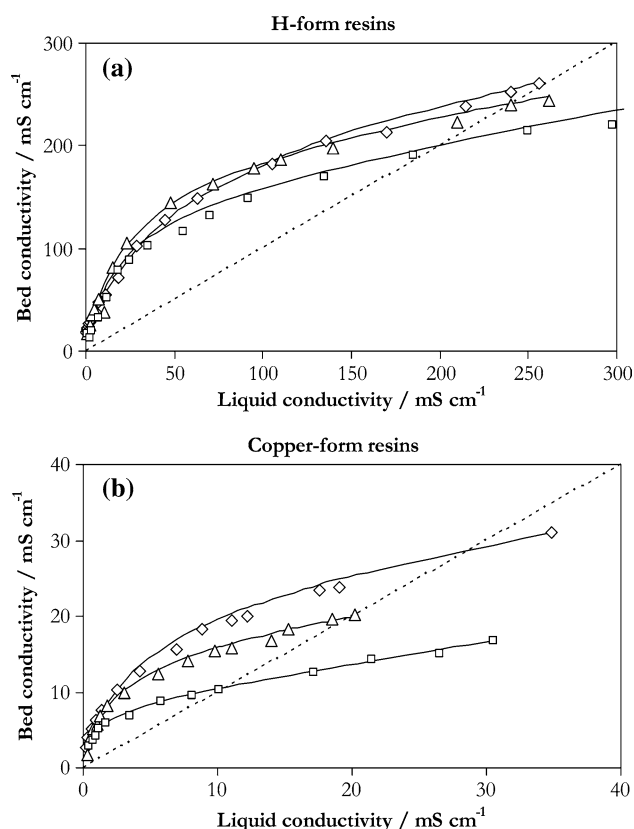


Fig. 2. Variation of the bed conductivity with the solution conductivity. (a) H⁺-form resins, (b) Cu²⁺-form resins. Experimental data: (◇) 50 WX 2%, (Δ) 50 WX 4%, (□) HCR-S 8%. Solid lines are for fitted variations.

electrolyte concentrations (Figure 2), and the contribution of the liquid phase to the ion transport became more significant. At the isoconductivity point, the bed conductivity is equal to the solution conductivity. This point represents the conductivity of the corresponding ion exchange resin bed and the values obtained are given in Table 1.

3.3. Use of the plug-flow model

Fitting of the experimental curves to the model gave access to the parameter values reported in Table 1. Agreement between experimental data and fitted variations was generally good. Figure 3 schematically illustrates the ion flux within the resin beds, both horizontally and vertically, following the electrical circuit shown in Figure 1. In Figure 3, the current flows in the vertical direction. Grey-filled blocks represent the solid resin phase contribution whereas white blocks correspond to the solution phase. From the left, they illustrate transport through both the solution in contact to the resin phase, the solid phase, and the solution phase, respectively.

For Dowex HCR-S 8%, best fittings were obtained with c values different from 0.28, holding for the two other resin grades, (Table 1). For all resins, the current

is mainly transported through the alternating layers of particles and solution. Therefore, the ion exchange resins are more conductive than the solution to be treated, as expected.

The conductivity parameters were used for prediction of the conductivity of resin beds impregnated with the solutions treated in EDI experiments: the solutions were 1.58 and 3.16 mol m⁻³ copper sulphate media (i.e. 100 and 200 ppm Cu²⁺ species, acidified with sulphuric acid, and with a pH near 3.2. The conductivity of the solutions was 1.08 and 1.13 mS cm⁻¹. For the 100 ppm Cu solution, the bed conductivity was determined at – 23.95, 17.74 and 13.71 mS cm⁻¹ for H⁺ form resins, with DVB at 2, 4 and 8 %, and – 6.35, 5.86 and 4.44 mS cm⁻¹ for the same resins in the Cu²⁺ form. For mixed beds of H⁺ and Cu²⁺ resins, the conductivity of the solid phase is a combination of the conductivities of the two present forms, assuming a parallel circuit of H⁺ and Cu²⁺ resistances:

$$\bar{\kappa} = \bar{\kappa}_{\text{H}^+} (1 - \bar{X}_{\text{Cu}^{2+}}) + \bar{\kappa}_{\text{Cu}^{2+}} \bar{X}_{\text{Cu}^{2+}} \quad (5)$$

where $\bar{X}_{\text{Cu}^{2+}}$ is the fraction of copper form resin in the bed, the rest being in H⁺-form. The variation of the bed conductivity with its composition was investigated as described in the following section.

Table 1. Conductivity of the resin particles and parameters involved in the plug flow model

Parameter	Dowex 50 WX 2%		Dowex 50 WX 4%		Dowex HCR-S 8%	
	H ⁺	Cu ²⁺	H ⁺	Cu ²⁺	H ⁺	Cu ²⁺
$\bar{\kappa}/\text{mS cm}^{-1}$	265	29	242	20	200	10
a	0.651	0.633	0.674	0.663	0.657	0.633
b	0.069	0.087	0.046	0.057	0.033	0.121
c	0.28	0.28	0.28	0.28	0.31	0.246
d	0.835	0.851	0.906	0.890	0.911	0.874
e	0.165	0.149	0.094	0.110	0.089	0.126

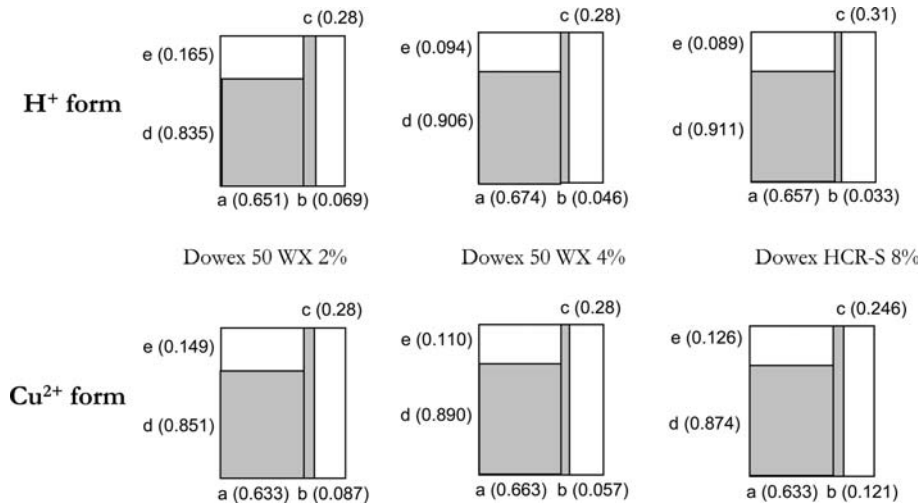


Fig. 3. Representation of the ratio between the solid and solution phases; grey blocks are solid phases and white blocks are solution phases. Current flows vertically in the representation.

4. Estimation of the bed conductivity from EDI experiments

The objective of this study was to compare the predicted variations of the bed conductivity with the fraction of copper-form resin, $\bar{X}_{\text{Cu}^{2+}}$, with the bed conductivities which can be drawn from EDI runs in short resin columns.

4.1. Electrodeionisation with short resin columns

The above resins were used for the treatment of dilute, weakly acidified copper sulphate solutions at room temperature. The cell used was a three-chamber system, and the packed bed, 100 mm high, 10 mm broad and 15 mm thick, was inserted between two electrode compartments filled with 0.5 M sulphuric acid [5]. The dimensions of the cell are given in Figure 4. The sulphuric solutions were circulated batchwise and copper ions accumulated in the bed and in the cathode liquid during the run. For the sake of a more uniform composition of the resin, only a short bed of Dowex particles, 15 mm high, was situated between two inert resin beds of the same particle size, each of them 42.5 mm high (Figure 4). As done previously for ion-exchange investigations with short resin columns [9], the short resin bed was used for thorough investigation of the effects of the operating parameters [10], with a restricted reduction in copper ion concentration in the fed solution.

Acidified copper sulphate solutions with composition given in Section 3.3 were treated. Treatment was carried out in single-pass operations through galvanostatic runs with current densities varying from 8 to 20 mA cm⁻², i.e. currents in the range 12–30 mA. The flow rate

through the bed was fixed at 10 cm³ min⁻¹, the cell voltage, U_{cell} , was recorded regularly. Unless specified, the resin was initially in the H⁺-form, and the transient loading of Cu²⁺ ions in the resin occurred for approximately 2 h. After loading of the resins bed, treatment of the copper sulphate solution was achieved by the simultaneous sorption of Cu²⁺ ions from the fed solution and ion migration to the cathode chamber, i.e. through the packed bed then the membrane [10]. The solutions from the electrode chambers, and that leaving the central bed were collected every 15 min and analysed. The depletion in copper ions varied from 10 to 30% depending on the applied current. Mass balances on copper species led to the time variation of the mole fraction of copper in the bed. Analysis of the resin bed at the end of the batch run showed that mass balances usually held within 10% and confirmed the values for the copper fractions in the resins at intermediate points.

4.2. Calculation of the bed conductivity from experimental data

The bed conductivity was calculated from the primary distribution of potential and current density in the overall cell. Since overpotentials and the open circuit voltage were not accounted for in such distributions, these contributions had to be subtracted from the overall cell voltage, which was generally written as:

$$U_{\text{cell}} = U_0 + \eta_a + |\eta_c| + U_{\text{ohm}} \quad (6)$$

where U_0 is the cell voltage at zero current, η_a and η_c , the anode and cathode overvoltage, and U_{ohm} represents the sum of the ohmic drops in the various cell chambers ($U_{\text{ohm},a} + U_{\text{ohm},c} + U_{\text{ohm},\text{bed}}$). The membrane resistances were neglected here. For this purpose, the electrodeion-

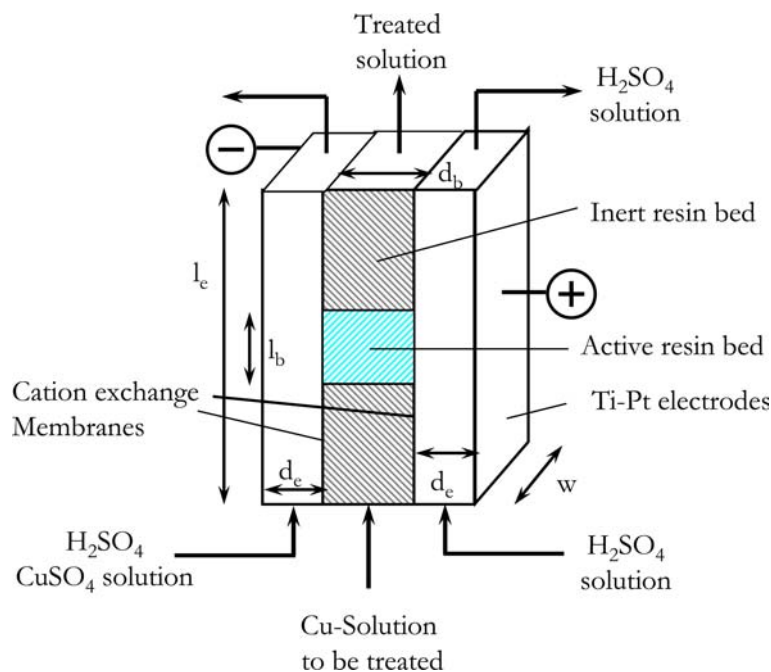


Fig. 4. Schematic view of the EDI cell, with the 15 mm resin bed for treatment of copper sulphate solutions.

isation cell was modified by replacing the particle beds by the sulphuric solution used in the electrode chambers: in this case, the current lines are perpendicular to the electrodes, and the cell voltage, U_{empty} , was therefore written as:

$$U_{\text{empty}} = U_0 + \eta_a + |\eta_c| + (R_a + R_c + R_{\text{central}})I \quad (7)$$

where the various resistances were calculated from the conductivity of the sulphuric solution, κ_e , and the dimensions of the chambers:

$$R_a = R_c = \frac{1}{\kappa_e} \frac{d_e}{w \cdot l_e} \quad (8a)$$

$$R_{\text{central}} = \frac{1}{\kappa_e} \frac{d_b}{w \cdot l_e} \quad (8b)$$

For currents ranging from 20 to 200 mA, cell voltage E_{empty} could be fitted by the relation

$$U_{\text{empty}}(V) = 1.6145 + 32.7I \quad \text{where } I \text{ is in A} \quad (9)$$

The potential difference, Φ_{cell} , to be considered for primary distributions was deduced as:

$$\begin{aligned} \Phi_{\text{cell}} &= U_{\text{ohm},a} + U_{\text{ohm},c} + U_{\text{ohm},\text{bed}} \\ &= U_{\text{cell}} - U_{\text{empty}} + (R_a + R_c + R_{\text{central}})I \end{aligned} \quad (10)$$

It can be shown that the equivalent conductivity of the inert beds filled with the dilute copper solution was far below those of the active compartment, and of the electrode chambers, κ_e . Therefore, the two regions upstream and downstream of the active bed were considered inactive, and the integration was conducted in the domain shown in Figure 5. Two symmetry planes were defined: a vertical plane at $x = d_e + d_b/2$, and a horizontal plane dividing the bed into two sections each being $l_b/2 = 7.5$ mm high. Current distributions were calculated in one fourth of the initial domain (Figure 5): one fourth of the bed, of overall conductivity κ_b , and half of one electrode chamber ($\kappa_e = 0.21 \text{ S cm}^{-1}$).

Integration of the Laplace equation was carried out in the two-dimensional domain

$$\frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial^2 \Phi}{\partial y^2} = 0 \quad (11)$$

using Femlab™ software for various compositions of the resin bed and experimental couples ($I-U_{\text{cell}}$). The following boundary conditions were considered (Figure 5):

$$\begin{aligned} \Phi(0, y) &= 0 \quad \text{for } 0 \leq y \leq l_e/2 \\ \Phi(d_e + d_b/2, y) &= \Phi_{\text{cell}}/2 \quad \text{for } 0 \leq y \leq l_b/2 \\ \partial \Phi / \partial x &= 0 \quad \text{for } x = d_e + d_b/2 \text{ and } 0 \leq y \leq l_b/2 \\ \partial \Phi / \partial n &= 0 \quad \text{on the inert walls} \end{aligned} \quad (12)$$

where n is the coordinate normal to the wall. Current density fields were deduced from the potential field in the two integration zones, using a postulated value for the bed conductivity, κ_b^{est} . Integration of the current

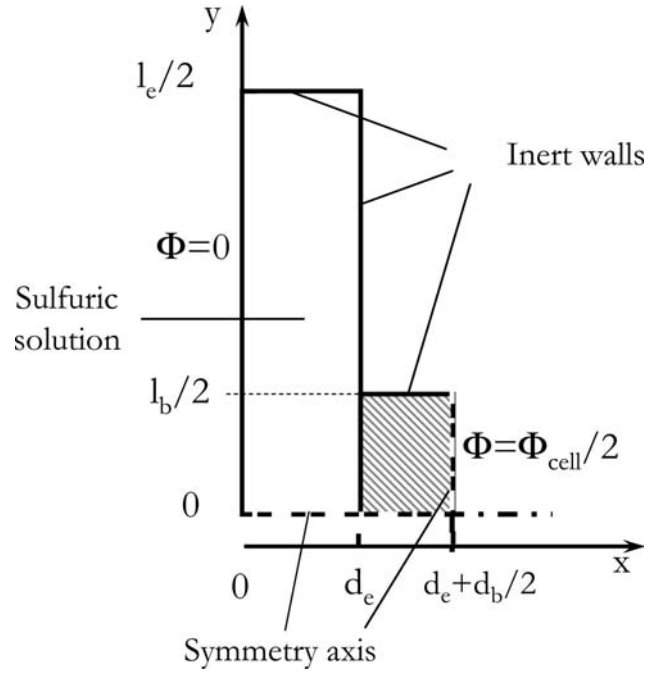


Fig. 5. Integration domain of the Laplace equation: $1/4$ of the electrodeionisation cell provided with a 15 mm high resin bed. ($d_e = 5$ mm, $d_b = 15$ mm, $l_b = 15$ mm, $l_e = 100$ mm).

density along the cathode ($\Phi = 0$) and along the vertical wall in the resin bed, yielded close estimates for the cell current, I_{est} , as expected. A new estimate for the bed conductivity was obtained from the estimated and applied currents, I_{est} and I respectively:

$$\kappa_b^{\text{new}} = \kappa_b^{\text{est}} \frac{I}{I_{\text{est}}} \quad (13)$$

Satisfactory convergence was usually obtained after a few iterations, yielding the bed conductivity for the ($I-U_{\text{cell}}$) couple considered. It can be observed that, because the bed conductivity was far below κ_e , the bed conductivity could be approximated within 10% from the approximate resistance (Φ_{cell}/I).

4.3. Calculation of the theoretical bed conductivity

Due to ion-exchange and electromigration, the liquid conductivity varied along the bed axis. The bed conductivity was calculated using relation (1), and taking into account both the actual conductivity of the solid and the local variations of κ , as explained below. The bed of resin was assumed to be of uniform composition. With respect to the liquid phase, the resin bed was modelled as a plug flow reactor, with negligible dispersion. The flux of copper ion transferred through the membrane was assumed to be proportional to the copper species concentration in the bed, and to the current density, regardless of the concentration in the liquid. Due to the zero-order kinetic law postulated here, the copper concentration decreased linearly with abscissae x in the bed. Because of the ion exchange stoichiometry,

the concentration of H^+ increased linearly with x . For very dilute solutions, the conductivity of the liquid is equal to the weighted sum of the partial ion conductivities, each of them being proportional to the concentration of the ion considered. Therefore, the linear concentration profiles are to correspond to linear conductivity profiles in the packed bed, with length l_b :

$$\kappa(x) = \kappa_{in} + (\kappa_{out} - \kappa_{in}) \frac{x}{l_b} \quad (14)$$

where conductivities κ_{in} and κ_{out} are the inlet and outlet conductivities. Plug flow was approximated by the cascade of n beds of uniform composition, with height Δx , so that $l_b = n\Delta x$. The overall bed was modelled as a circuit of n electrical resistances in parallel, because of the cross-flow configuration of the system. Therefore:

$$\frac{1}{R_b} = \sum \frac{1}{R_{x,\Delta x}} = \sum \kappa_b(x) \frac{w \cdot \Delta x}{d_b} \approx \int_0^{l_b} \kappa_b(x) \frac{w}{d_b} dx \quad (15)$$

The average bed conductivity, $\kappa_{b,av}$ was defined from the overall bed resistance, R_b

$$R_b = \frac{1}{\kappa_{b,av} w \cdot l_b} \quad (16)$$

leading to:

$$\kappa_{b,av} = \frac{1}{l_b} \int_0^{l_b} \kappa_b(x) dx \quad (17)$$

It can be observed that the axial variation of the bed conductivity was not accounted for in the calculations of primary distributions (Section 4.2), which allow the average conductivity to be estimated.

5. Comparison of the two approaches and discussion

Long term treatments of solutions, with H^+ -form resins at $t=0$, were first considered. In the initial stages, for low values of copper mole fraction in the resin, Figure 6

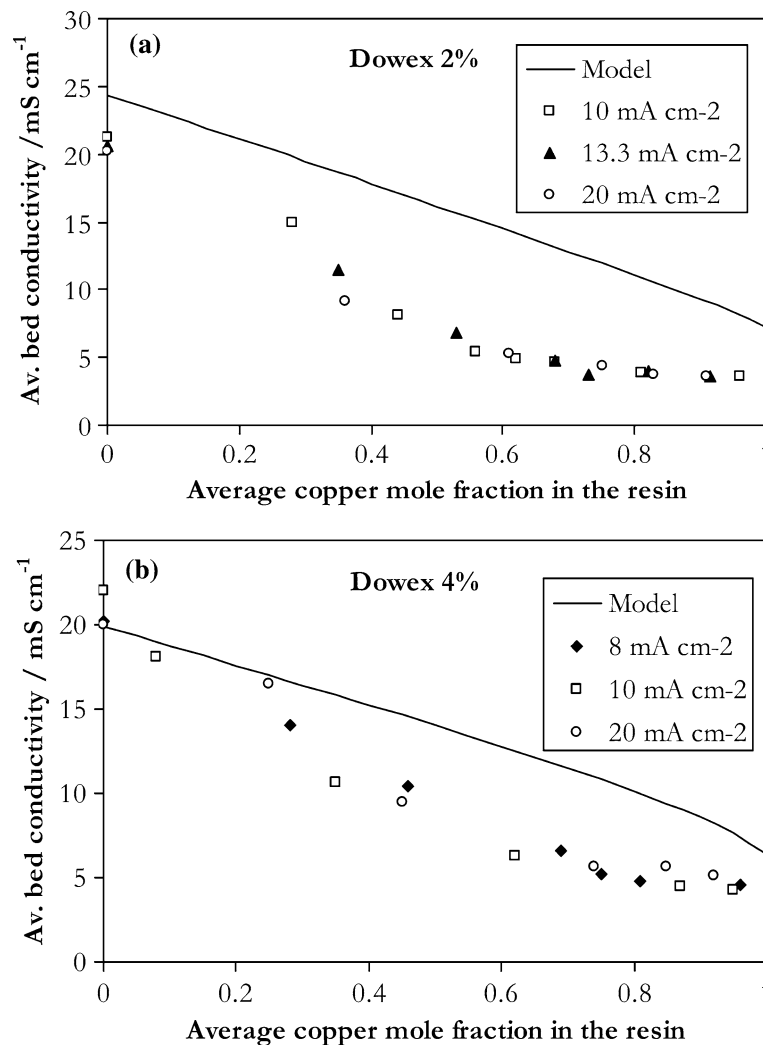


Fig. 6. Variation of the bed conductivity with the copper ion mole fraction in the resin (a) Dowex 2%, (b) Dowex 4%. Solution: 1.58 mol m^{-3} copper sulphate at pH 3.2. Solid line, predicted variation after Wyllie's model; symbols: conductivity estimates from the cell voltage for continuous treatment of the above solutions, with H-form resin at $t=0$.

shows good agreement between the theoretical predictions of κ_b , and the “experimental” values, i.e. deduced from the potential distributions and the cell voltage values. However, after the first sampling (15 min), the “experimental” conductivity decreased far more rapidly than the conductivity calculated with Wyllie’s model versus the copper mole fraction. For \bar{X}_{Cu} larger than 0.3, the experimental values were nearly two times smaller than the theoretical ones, whatever the current applied and the resin grade. The assumptions made in the model development were thoroughly examined as follows.

During the runs, a flat front appeared in the small resin bed in the first 20 min or so, due to the progressive loading by Cu^{2+} species; the assumption of uniform resin bed may therefore be questionable. However, the appearance of the bed was homogeneous after the transient period, as confirmed by analysis of various

parts of the bed in test experiments. The conductivity determined from the potential distribution after complete saturation of the bed, within 90 min, were also far below the theoretical values calculated with $\bar{X}_{Cu} = 1$, which suggested the occurrence of side-electrical phenomena, as discussed below.

Complementary experiments using partially impregnated 4% DVB resins were carried out for 30 min, with 200 ppm Cu^{2+} solutions at pH 3.2. The cell voltage remained roughly constant and the conductivity data deduced from potential distributions was found to be 20% lower than the values calculated by the plug-flow model (Figure 7). In another experiment conducted with pure Cu-form resins ($\bar{X}_{Cu} = 1$) at $t=0$ percolated with the above solution, the cell voltage was observed to increase after 20–30 min, resulting in values of apparent conductivity reduced by 50% within 2 h (Figure 8). The two sources of data showed (i) the fair validity of the

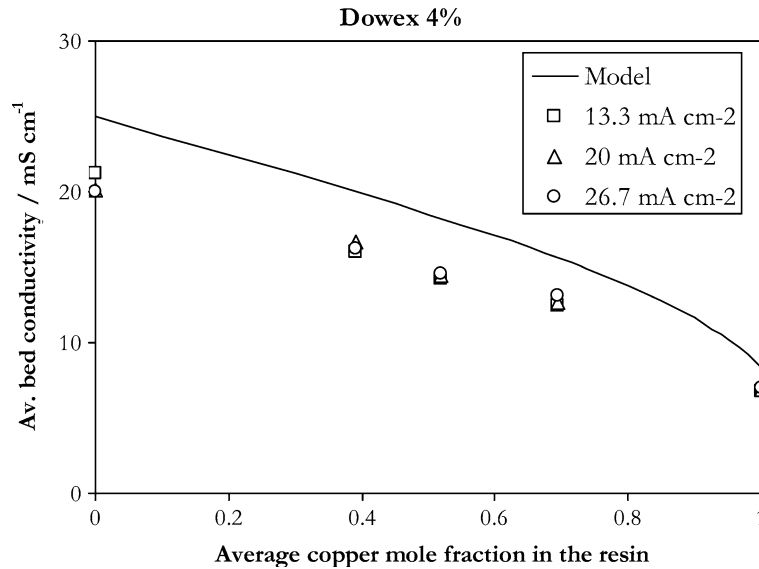


Fig. 7. Variation of the bed conductivity with the copper ion mole fraction in the 4% Dowex resin. Solution: 3.16 mol m^{-3} copper sulphate at pH 3.2. Solid lines, predicted variation after Wyllie’s model; symbols: conductivity estimates from the cell voltage for 20-min treatment of the above solution, and starting with various copper mole fractions in the resin.

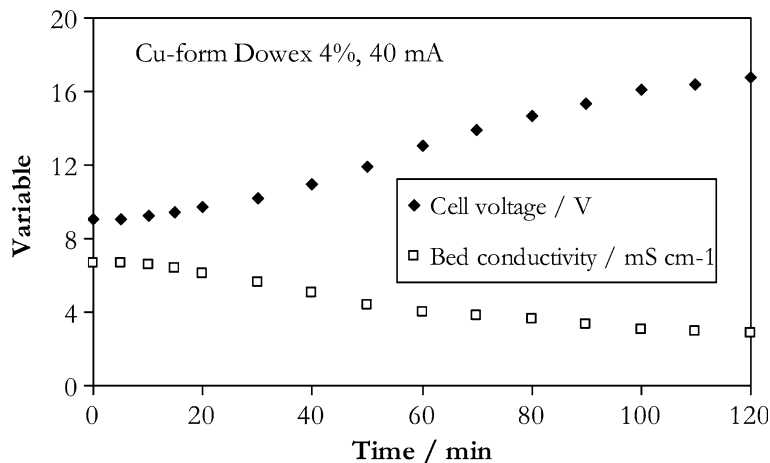


Fig. 8. Time variation of the cell voltage and of the overall conductivity of the bed for treatment of 3.16 mol m^{-3} copper sulphate solution at pH 3.2, and starting with Cu^{2+} -form resin (Dowex 4%).

electrical model for ion-exchanging beds, (ii) the unexpected increase in cell voltage, regardless of the ionic form of the resins. The latter phenomenon may be due to local deposition of impurities e.g. metal hydroxide, at the resin surface and, possibly also on the membrane surface. This point requires more thorough investigation. Earlier experiments of electrodeionisation of dilute acidic copper chloride solutions, conducted for 70 h [11] led to voltages nearly three times larger than the experimental value expected from the resin conductivity measured by impedance spectroscopy, confirming the occurrence of side phenomena.

6. Conclusion

The ohmic drop in conducting beds of ion-exchange resins was determined using two techniques. Electrical conductivity of resin beds in electrolyte solutions was shown to obey the two-phase plug flow model developed decades ago by Wyllie et al. In particular, for dilute solutions, the solid–liquid interaction term prevails, leading to bed conductivity far higher than that of the electrolyte solution. Parameters of the model were determined for Dowex resins of different degrees of cross-linking, allowing first estimation of the electrical conductivity of ion exchange resin beds. Using the voltage of the EDI cell during treatment of dilute copper sulphate solutions, primary distributions of potential led to a second estimation of the bed conductivity, which was plotted versus the copper mole fraction in the resin.

Agreement with application of Wyllie's model was good for short-term operations, only. Use of the bed conductivity deduced from Wyllie's model for prediction of the voltage of EDI cells is, however, hindered by side phenomena, which might be the progressive fouling of the membranes or of the resin particle surface, resulting in significant increases in cell voltage. This phenomenon, observed for acidic solutions of copper chloride or sulphate, requires further investigation.

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